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ANALYTICAL REFERENCE SERVICE TRAINING PROGRAM. SAMPLE TYPE IV, AIR-INORGANIC

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

December 1958

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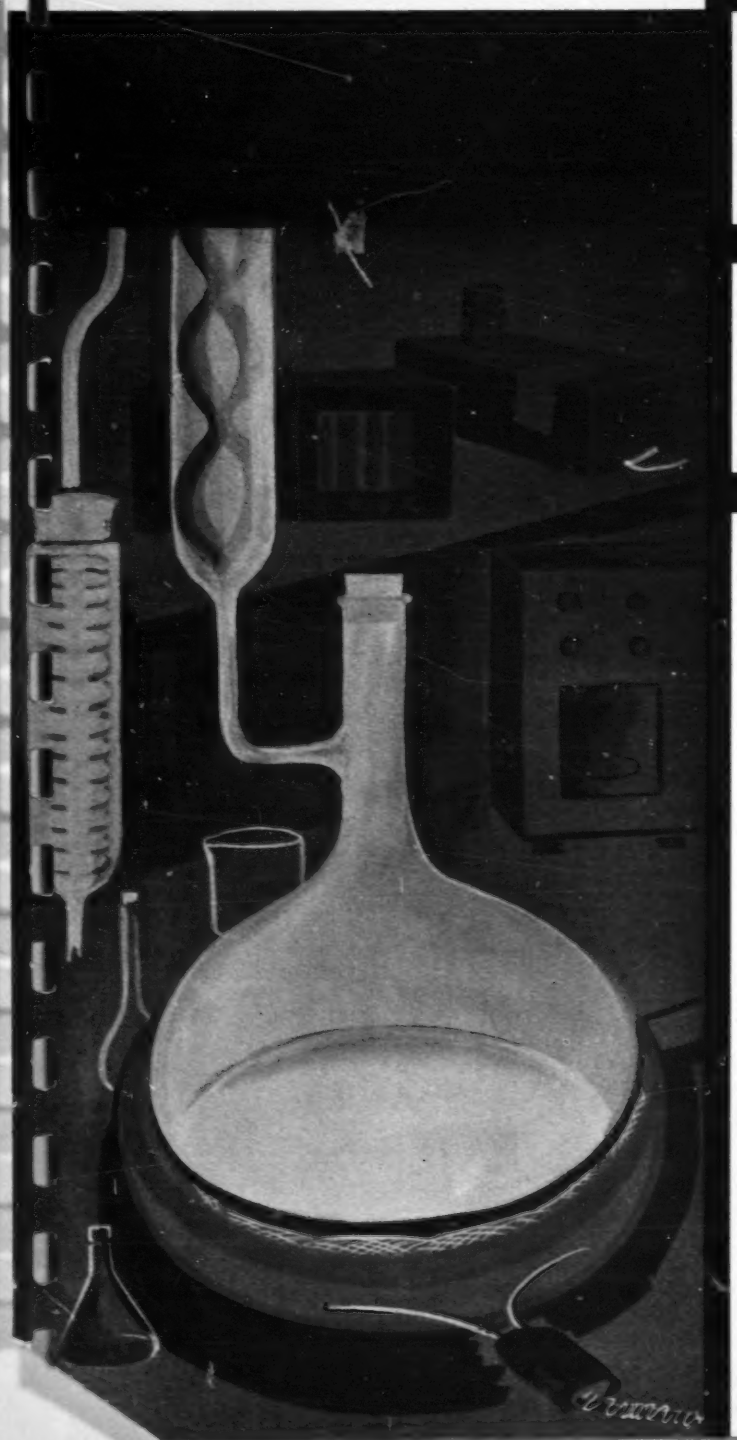
analytical reference service



training program

Robert A. Taft

Sanitary Engineering Center

Cincinnati, Ohio

U. S. Department of Health, Education, and Welfare

· Public Health Service

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ANALYTICAL REFERENCE SERVICE

INTRODUCTION

The Analytical Reference Service conducted by the Sanitary Engineering Center has as its primary goal the evaluation of laboratory methods in the field of sanitary engineering. The Reference Service itself is a voluntary association of member organizations responsible for the conduct of laboratory programs. The evaluations are obtained by the cooperative efforts of the members in the analysis of identical samples.

This mechanism provides:

1. A statistical evaluation of procedures, including precision and accuracy.

2. An opportunity for a participant to compare his laboratory procedures and results with other laboratories having similar responsibilities.

3. An exchange of information regarding weaknesses of currently approved methods.

4. Evidence regarding methods requiring further development or perhaps entirely new approaches.

5. A framework for broad-scale evaluation of new analytical methods.

PLAN OF OPERATION

Initially, efforts are being directed toward the chemical examination of water. The scope of the program will be broadened gradually to include other types of examinations and other media.

Using the most refined grade of chemicals available, samples are prepared containing measured amounts of the desired constituent. Decisions as to the qualitative makeup of any particular sample follow suggestions from the members and from the staff of the Sanitary Engineering Center.

After a sample is designed and prepared, a notice announcing its availability and qualitative makeup is sent with a self-addressed reply card to member organizations. An affirmative reply initiates immediate shipment of a portion of the described sample. Results are requested within some reasonable period, usually sixty days.

REPORTING OF RESULTS AND COMMENTS

Data are returned to the Sanitary Engineering Center on forms supplied with the sample. Space is provided on the forms for numerical values and a narrative critique of analytical procedures used.

The results obtained by the cooperating laboratories are compiled as in the accompanying report. From examination of the combined data, it is hoped that reliable estimates may be made of the accuracy and precision of the methods employed.

All laboratories are strongly encouraged to supply comments on the analytical methods they use. A complete log of pertinent details, including difficulties, modifications, sources of error, and other factors, is extremely valuable. Such a compilation of comments represents an exchange of ideas and opinions that is a significant part of the final report.

H. P. Kramer
Chief, Training Program

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ANALYTICAL REFERENCE SERVICE

MEMBERS AS OF FEBRUARY 1, 1959

State Agencies

Arizona State Department of Health
Arkansas State Board of Health
California Department of Water Resources (Sacramento)
California Department of Water Resources (San Bernardino)
California Department of Water Resources (Riverside)
California State Department of Public Health (Berkeley)
California State Department of Public Health (Los Angeles)
Colorado State Department of Public Health
Connecticut State Department of Health
Florida State Board of Health
Territory of Hawaii Department of Health
Idaho State Board of Health
Illinois State Water Survey Division
Kentucky State Department of Public Health
Louisiana State Department of Health
Maryland State Department of Health
Maryland Water Pollution Control Commission
Michigan Department of Health
Minnesota State Department of Health
Missouri Department of Public Health and Welfare
Montana State Board of Health
Nebraska State Department of Health
New Hampshire Water Pollution Commission
New Jersey State Department of Health
New Mexico Department of Public Health
New York State Conservation Department
New York State Department of Health
North Carolina State Board of Health
Onio Department of Health
Oregon State Board of Health
Pennsylvania Department of Health
Rhode Island and Providence Plantations Department of Health
South Carolina State Water Pollution Control Authority
South Dakota State Department of Health
Tennessee Stream Pollution Control Board
Texas State Department of Health
Utah State Department of Health
Vermont Water Conservation Board
Vermont Department of Health
Virginia Water Control Board
Washington State Department of Health
West Virginia State Water Commission

Municipal Agencies

Los Angeles Department of Water and Power
Chicago Department of Water and Sewers
Metropolitan Water District of Southern California

Federal Agencies

U.S. Army Environmental Health Laboratory, Maryland
Sanitary Engineering Division, 13th Naval District
U.S. Department of the Interior, Geological Survey
Columbus, Ohio
Sacramento, California
Washington, D.C.
U.S. Department of the Interior, Bureau of Reclamation
Denver, Colorado

Universities

Rutgers University, Department of Sanitation
Purdue University. Department of Chemistry
Georgia Tech, Department of Applied Biology
University of Pittsburgh, Graduate School of Public Health
Case Institute of Technology
Department of Civil Engineering and Engineering Mechanics

Industrial

National Aluminate Corporation
Monsanto Chemical Company

PARTICIPANTS IN THIS STUDY OF SAMPLE TYPE IV

(Distributed May, 1958)

Arizona State Department of Health
Baltimore City Health Department
Bay Area Air Pollution Control District (San Francisco)
California State Department of Public Health (Berkeley)
California State Department of Public Health (Los Angeles)
Connecticut State Department of Health
Illinois State Water Survey Division
Los Angeles Air Pollution Control District
Louisiana State Department of Health
Minnesota State Department of Health
Missouri Department of Public Health and Welfare
Montana State Board of Health
New Hampshire Water Pollution Commission
New Mexico State Department of Public Health
Oregon State Board of Health
Rutgers University, Department of Sanitation
South Dakota State Board of Health
Texas State Department of Health
Utah State Department of Health
Vermont Water Conservation Board

LIST OF ANALYTICAL REFERENCE SERVICE SAMPLES WHICH HAVE BEEN DISTRIBUTED AND ON WHICH REPORTS HAVE BEEN COMPLETED

SAMPLE TYPE I AND IA

(Mineral, Water) analyzed for calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium and potassium.

SAMPLE TYPE II

(Heavy Metals, Water) analyzed for copper, cadmium, aluminum, chromium, iron, lead, manganese, and zinc.

SAMPLE TYPE III

(Fluoride, Water) analyzed for fluoride in the presence and absence of interferences with and without distillation, using a specified procedure.

SAMPLES WHICH HAVE BEEN DISTRIBUTED AND WHICH ARE NOW IN THE PROCESS OF STUDY

SAMPLE TYPE V

(Radiological, Water) processed and counted for measurement of gross beta activity.

SAMPLE TYPE VI

(Surfactant, Water) analyzed for anionic materials in distilled, tap and raw river waters.

REPORT ON SAMPLE TYPE IV

Purpose of this Study

During the past fifty years, the number of community air pollution control programs in the United States has quadrupled. An increasing effort is evident in the attempt to identify and measure atmospheric pollutants. Adequate analytical procedures are an essential part of evaluation of atmospheric pollution problems. In veiw of the relatively low concentrations of contaminants in air, the methods chosen should meet rather rigorous standards of sensitivity and accuracy. This sample was prepared and distributed to assess the reliability and usefulness of current methodology in respect to four anions normally present in the atmosphere as particulate matter.

Filtration of large volumes of air is one widely used method for collecting airborne particulate matter. Since the initial analytical step, extraction of the filter, seemed to offer serious possibilities of variation in terms of efficiency, the sample was designed to evaluate this possibility. This was accomplished by preparing the sample in two parts; Part A, a solution containing known quantities of the four anions, and Part B, a filter impregnated with the same four anions.

Preparation of Sample

Part A: Solution

Substrate: Distilled water passed through a deionizing column

Chemicals: All reagents were ACS reagent grade taken from freshly opened bottles.

Part B: Filter

Substrate and chemicals were qualitatively identical to those used in Part A.

Exactly ten ml of a solution similar to that prepared for Part A was applied to a dry, rolled, 1106-B glass fiber filter web*. The filter was re-dried, inserted in a chemically clean culture tube and capped.

*The glass fiber filter webs used in this study were obtained from Mine Safety Appliances Inc., and were extracted continuously with boiling water for eight hours (Soxhlet). No chloride, fluoride, sulfate or nitrate could be chemically detected in the washed filters.

TREATMENT OF DATA

The twenty-one laboratories participating in this study reported a total of 166 analytical results based in most cases upon measurements in triplicate.

Statistical treatment of the data in this report is similar to that used in Type I (Mineral, Water) sample [1]. The choice of type of statistical analysis used have been governed by the limited number of data. For example, standard deviations were calculated only for those specific methods used by at least five laboratories.

The parameters used in the analysis of the data are:

1. average amount reported
2. range of the amounts reported
3. standard deviation
4. average percent deviation from amount added
5. range of the percent deviations from the amount added

[1] ARS #1 (Mineral, Water)

SULFATE

The data reported by the 21 participating laboratories have been divided into five groups according to the analytical method used. These results are summarized in Table 1 and shown graphically in Figure 1. The individual methods are listed in Table 5.

The variations observed in the analytical data on both the solution and filter fractions of the sample were similar. The average percent deviation from the amount added was 10.52% and 10.75% for the solution and filter samples respectively. The individual laboratory results ranged from -23.7 to 44.0% and -20.0% to 37.5% for the solution and filter samples respectively.

Only one of the methods used on the filter portion produced results having a standard deviation of less than 10%. Method B, a turbidimetric procedure had a standard deviation of $\pm$ 1.00 mg/filter, or 6.25% of the amount added.

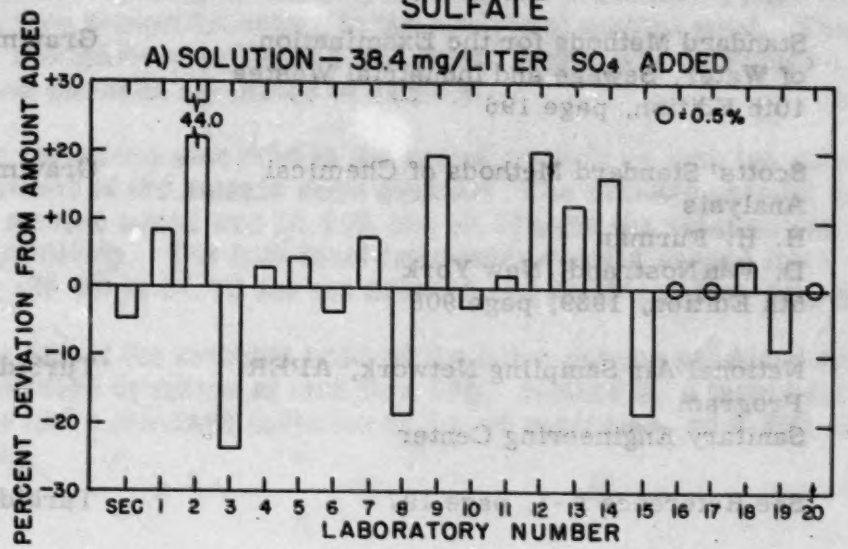
SUMMARY OF RESULTS

TABLE I - SULFATE

Type of Sample	Amount Added	Method	Number of Results Reported	Amount Reported			Percent Deviation From Amount Added	
				Average	Range	Standard Deviation	Average	Range
A) Solution	38.4 mg/liter	A	8	39.68	31.3 - 45.9	±4.70	9.25	-18.5 to +19.3
		B	6	35.22	29.3 - 39.9	±4.17	9.70	-23.7 to + 3.9
		C	5	43.42	39.0 - 55.3	±6.72	13.08	+ 1.6 to +44.0
		D	1	37	----------	-----	-3.6	----------
		E	1	46	----------	-----	+19.8	----------
		Overall	21	39.47	29.3 - 55.3	±5.73	10.52	-23.7 to +44.0
B) Filter	16.0 mg/filter	A	7	16.47	12.8 - 20.5	±2.41	10.81	-20.0 to +28.1
		B	6	15.02	13.9 - 16.6	±1.00	7.40	-13.1 to + 3.8
		C	6	16.63	14.0 - 22.0	±2.28	13.97	-12.5 to +37.5
		D	1	14.0	----------	-----	12.5	----------
		E	1	17.5	----------	-----	9.4	----------
		Overall	21	16.03	12.8 - 22.0	±2.28	10.75	-20.0 to +37.5

FIGURE 1

ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE IV (AIR INORGANIC)
SULFATE



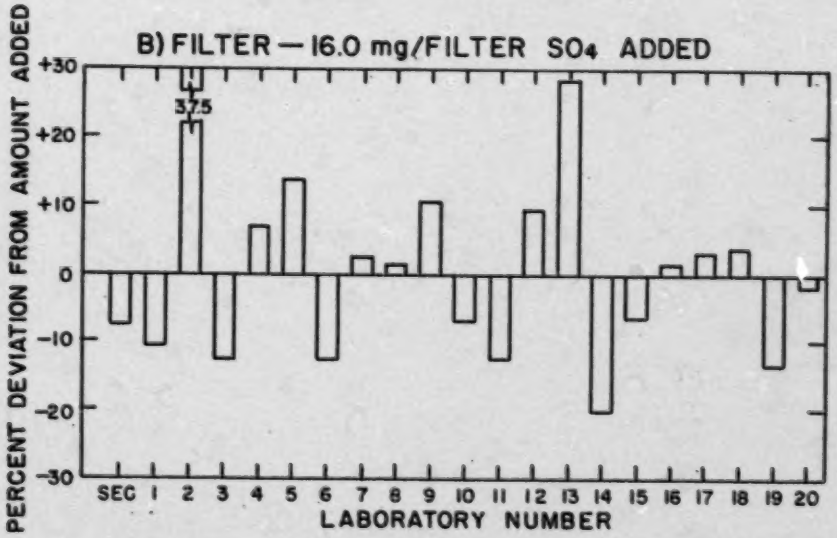
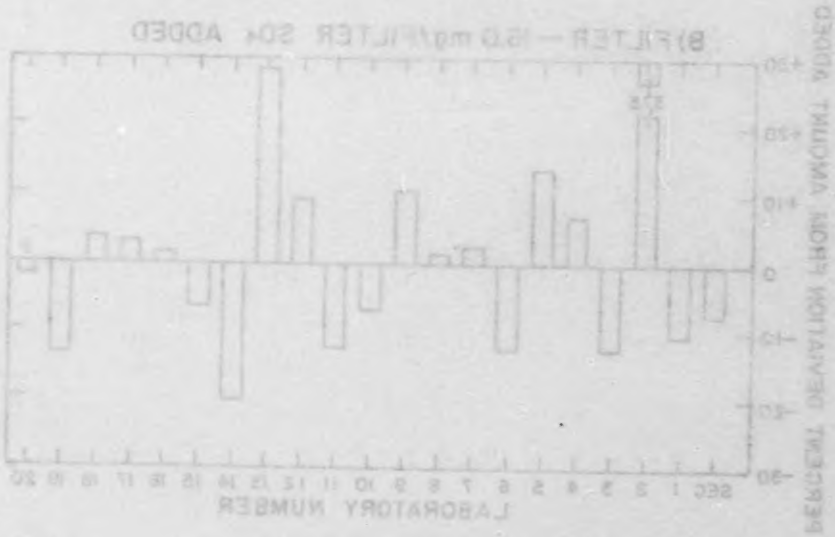


TABLE 5

KEY TO METHODS OF ANALYSIS FOR SULFATES

CODE	REFERENCE	METHOD
A-1	Standard Methods for the Examination of Water, Sewage and Industrial Wastes 10th Edition, page 196	Gravimetric
A-2	Scotts' Standard Methods of Chemical Analysis H. H. Furman D. Van Nostrand, New York 5th Edition, 1939, page 908	Gravimetric
B	National Air Sampling Network, APER Program Sanitary Engineering Center	Turbidimetric
C	See Reference A-1, page 197	Turbidimetric
D	Unidentified	
E	Determination of Sulfate Betz Indicator, 26, (February 1957)	Turbidimetric



COMMENTS ON SULFATE METHOD

Lab. 1 — Turbidimetric method has given better results for us than the titrimetric method which has never given a satisfactory endpoint. With a better endpoint, we would prefer a titrimetric method. We have not found the stirring conditions to be critical as is implied in the Standard Methods procedure.

(METHOD C)

Lab. 2 — The turbidimetric method worked very well at this concentration and gave consistent results.

(METHOD C)

Lab. 3 — No comments. (METHOD B)

Lab. 4 — No comments. (METHOD A-1)

Lab. 5 — We have had very reproducible results with this method. After adding the barium chloride crystals, we shake on the platform shaker for one minute, allow sample to set 4 minutes and shake again for 15 seconds. Using these time intervals, we have had excellent results on our recovery studies.

(METHOD C)

Lab. 6 — No comments. (METHOD D)

Lab. 7 — No comments. (METHOD C)

Lab. 8 — No comments. (METHOD A-1)

Lab. 9 — No comments. (METHOD A-2)

Lab. 10 — After addition of barium chloride crystals (250 mg), each tube was capped tightly and mixed gently by inversion for 30-40 seconds. Before placing the tube in the spectrophotometer, any microbubbles adhering to the wall of the tube were dislodged by tapping the tube sharply with a wooden lead pencil. The suspension was quite stable for more than one hour (70-80 min).

(METHOD B)

Lab. 11 — See Fluorides. (METHOD C)

Lab. 12 — Satisfactory at low dilutions. (METHOD E)

COMMENTS ON SULFATE (Cont'd)

Lab. 13 No comments. (METHOD A-1)

Lab. 14 For the analysis of air samples containing small concentrations, the accuracy of this method does not appear to be satisfactory. Other methods are being investigated. This method does not require an unusual amount of laboratory personnel time.

(METHOD A-1)

Lab. 15 This was the barium chloride turbidimetric method as furnished by the Sanitary Engineering Center for air pollution studies. The reproducibility of the standard curve was extremely difficult.

(METHOD B)

Lab. 16 I would have preferred using 500 ml of sample for sulfate determination, but this was not possible with the amount of sample sent for analysis. The calculations in the St. Methods -, 10th Ed. for determining sulfate are in error. According to St. Methods:

$$\text{mg/liter} = \frac{\text{mg } BaSO_4 \times 41.15}{\text{mls sample}}$$

Formula should be:

$$\text{mg/liter} = \frac{\text{mg } BaSO_4 \times 411.5}{\text{mls sample}}$$

or:

$$\text{mg/liter} = \frac{\text{mg } BaSO_4 \times 0.4115 \times 1000}{\text{mls sample}}$$

(METHOD A-1)

Lab. 17 No comments. (METHOD A-1)

Lab. 18 No comments. (METHOD B)

Lab. 19 My original plan was to use the barium chloranilate method for sulfate, but insufficient sample forced me to use the turbidimetric method recommended by the SEC for air samples.

(METHOD B)

Lab. 20 The method for the determination of water soluble sulfates in air particulate matter collected on glass fiber filter web, described by the Sanitary Engineering Center, was found satisfactory in this laboratory.

(METHOD B)

CHLORIDE

Six different groups of methods were used by the 21 laboratories participating in this study as shown in Table 2. The results are presented graphically in Figure 2.

The data demonstrate that the results with both the solution and the filter tend to be on the high side, with the filter results being significantly higher than those on the solution sample. See Figure 2. The average percent deviation from amount added was 12.15% and 19.05% for the solution and filter portions respectively.

Method G, the mercuric nitrate procedure showed in both the filter and solutions samples, standard deviations equal to or less than 10%.

Specifically, this was $\pm$1.32 mg/l and $\pm$0.60 mg/filter for the solution and filter portions respectively. The slight superiority of the mercuric nitrate method over other methods for chlorides has been previously noted in the report on Sample Type IA.

SUMMARY OF RESULTS

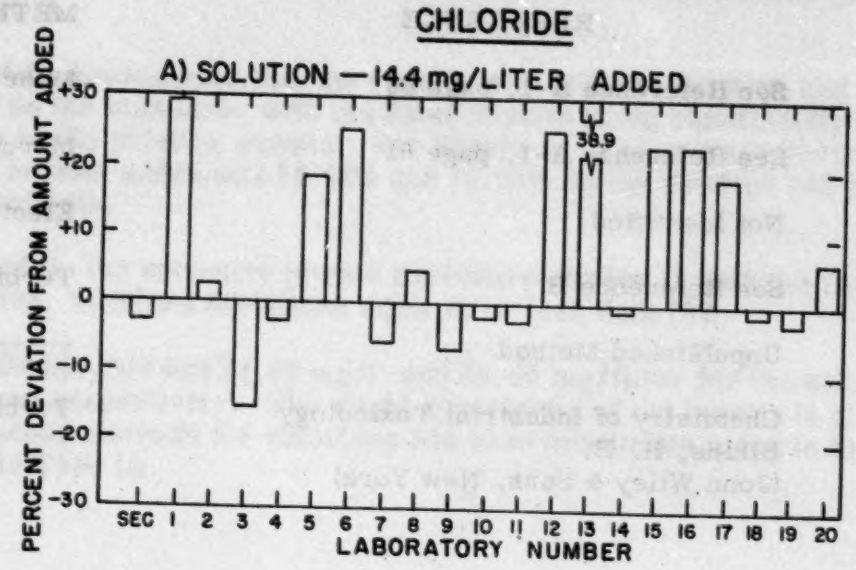
TABLE II - CHLORIDE

Type of Sample	Amount Added	Method	Number of Results Reported	Amount Reported			Percent Deviation From Amount Added	
				Average	Range	Standard Deviation	Average	Range
A) Solution	14.4 mg/liter	F	9	16.46	14.0 - 20.0	±2.30	15.98	-10.83 to +30.87
		G	5	14.75	13.4 - 17.0	±1.32	6.54	-14.93 to +10.07
		H	1	18.0	----------	-----	25.0	----------
		I	4	15.28	14.0 - 17.0	-----	8.18	-10.83 to +14.87
		J	1	13.6	----------	-----	5.6	----------
		K	1	12.2	----------	-----	15.3	----------
		Overall	21	15.56	12.2 - 20.0	±2.12	12.15	-15.3 to +30.87
B) Filter	6.0 mg/filter	F	9	7.37	5.5 - 9.8	±1.55	25.01	- 8.3 to +63.4
		G	5	6.56	6.0 - 7.2	±0.60	10.0	- 1.6 to +20.0
		H	1	8.0	----------	-----	33.4	----------
		I	4	6.83	6.5 - 7.7	-----	13.70	+ 8.4 to +28.0
		J	1	5.1	----------	-----	15.0	----------
		K	1	4.7	----------	-----	21.7	----------
		Overall	21	6.87	4.7 - 9.8	±1.29	19.05	-21.7 to +63.4

FIGURE 2

ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE IV (AIR INORGANIC)

CHLORIDE



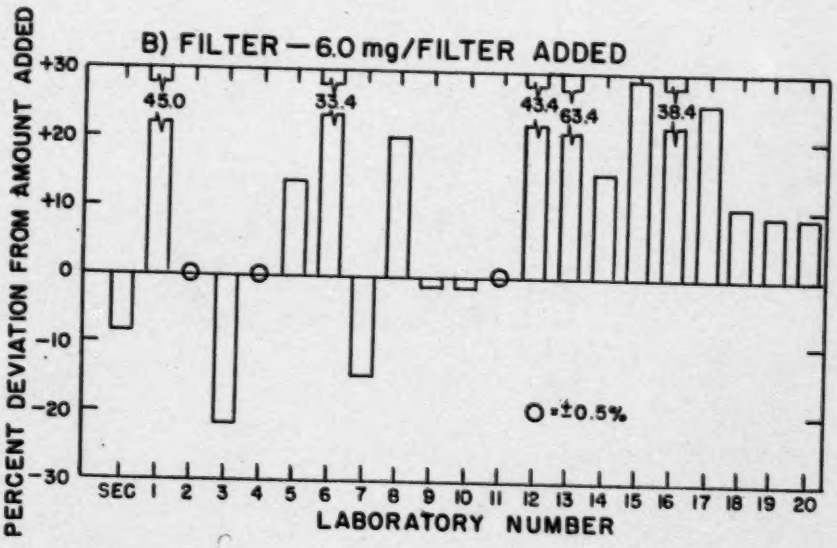


TABLE 6

KEY TO METHODS OF ANALYSIS FOR CHLORIDES

CODE	REFERENCE	METHOD
F	See Reference A-1, page 60	Mohr
G	See Reference A-1, page 61	Mercuric Nitrate
H	Not Identified	Electrotitrimetric
I	See Reference B	Turbidimetric
J	Unpublished Method	----------
K	Chemistry of Industrial Toxicology Elkins, H. B. (John Wiley & Sons, New York)	Turbidimetric

COMMENTS ON CHLORIDE METHOD

Lab. 1	Method is quite satisfactory although considerable experience is required in order to judge the endpoint accurately.	(METHOD F)
Lab. 2	The Mohr method gave consistent results. The endpoint is difficult to see and the tendency is to overshoot the endpoint, thus giving high results.	(METHOD F)
Lab. 3	No comments.	(METHOD K)
Lab. 4	Chlorides are usually run in this lab by the Mohr method. The mercuric nitrate method seems to give a better endpoint than the Mohr method. It was noted however, that the diphenylcarbazone - bromphenyl blue mixed indicator left stains in the glassware, requiring special efforts for removal.	(METHOD G)
Lab. 5	No comments.	(METHOD G)
Lab. 6	No comments.	(METHOD H)
Lab. 7	No comments.	(METHOD J)
Lab. 8	No comments.	(METHOD G)
Lab. 9	No comments.	(METHOD G)
Lab. 10	No comments.	(METHOD F)
Lab. 11	See Fluorides.	(METHOD F)
Lab. 12	Accurate.	(METHOD F)
Lab. 13	No comments.	(METHOD F)
Lab. 14	The precision of this method is acceptable for air pollution work as endpoints are fairly definite.	(METHOD G)

COMMENTS ON CHLORIDE (Cont'd)

Lab. 15 Turbidimetric method as furnished by Sanitary Engineering Center using silver nitrate. We had some difficulty in reproducing our results over a period of several days.

(METHOD I)

Lab. 16 No comments. (METHOD F)

Lab. 17 No comments. (METHOD F)

Lab. 18 No comments. (METHOD I)

Lab. 19 Chloride ion was also determined turbidimetrically using silver nitrate. The indicator used was p-nitrophenol.

(METHOD I)

Lab. 20 The method for the determination of water soluble chlorides in air particulate matter collected on glass fiber filter web, described by the Sanitary Engineering Center, was found satisfactory in this laboratory.

(METHOD I)

FLUORIDE

As can be seen in Figure 3, sixteen of the nineteen participating laboratories reported results within plus or minus 10% of the amount present in the solution portion. At a concentration of 1.0 mg/l, this represents a high degree of competency by the cooperating laboratories. In the case of the filter portion, 16 out of 20 groups reported fluoride results on the low side, with 12 of the laboratories showing losses of more than 10%. Half of the laboratories had deviations greater than 20%.

These data indicate that the amount of fluoride added to the filter is not quantitatively recovered using present extraction techniques. It is very probable that some of the fluoride ions are strongly adsorbed on the glass fiber surfaces.

The Megregian-Maier and the Scott-Sanchis methods were most frequently used by the participants and are capable of accurate results as indicated by the results obtained on the solution portion. Other methods were not used frequently enough to furnish reliable statistical evaluation.

SUMMARY OF RESULTS

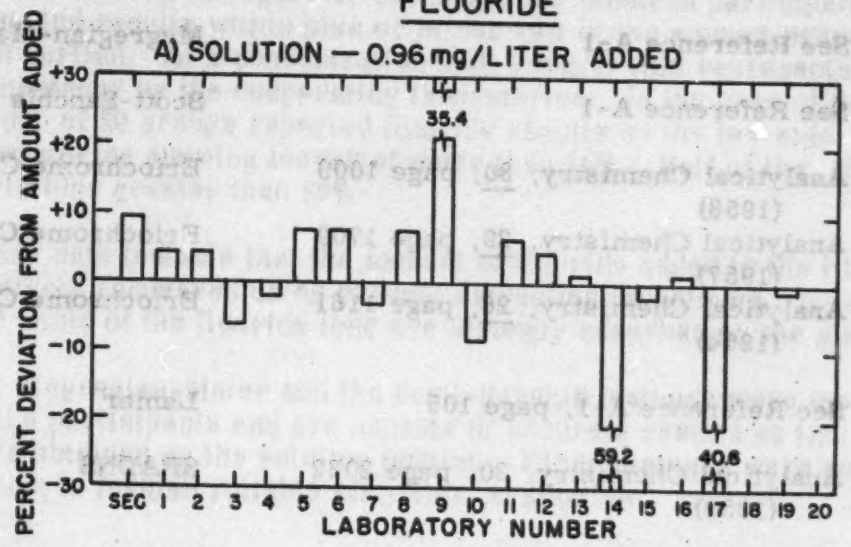
TABLE III - FLUORIDE

Type of Sample	Amount Added	Method	Number of Results Reported	Amount Reported			Percent Deviation From Amount Added	
				Average	Range	Standard Deviation	Average	Range
A) Solution	0.96 mg/liter	L	6	1.018	1.0 - 1.05	±0.046	6.10	+ 4.2 to + 9.4
		M	5	0.926	0.88 - 0.97	±0.040	3.94	- 6.2 to + 1.0
		N	2	0.940	0.93 - 0.95	------	2.05	- 3.1 to - 1.0
		O	2	0.995	0.97 - 1.02	------	3.65	- 3.0 to + 2.0
		P	1	1.03	----------	------	7.3	----------
		Q	2	0.750	0.20 - 1.30	------	57.30	-79.2 to +35.4
		R	1	0.57	----------	------	40.6	----------
		Overall	19	0.932	0.20 - 1.30	±0.221	12.12	-79.2 to +35.4
B) Filter	0.40 mg/filter	L	6	0.318	0.25 - 0.39	±0.048	20.41	-37.5 to - 2.5
		M	5	0.362	0.29 - 0.48	±0.073	17.50	-27.5 to +20.0
		N	2	0.400	0.38 - 0.42	------	5.0	- 5.0 to + 5.0
		O	2	0.350	0.30 - 0.40	------	12.50	-25.0 to 0.0
		P	1	0.25	----------	------	37.5	----------
		Q	2	0.320	0.19 - 0.45	------	32.50	-52.5 to +12.5
		R	1	0.20	----------	------	50.0	----------
		Overall	19	0.332	0.19 - 0.48	±0.079	20.92	-52.5 to +20.0

FIGURE 3

ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE IV (AIR INORGANIC)

FLUORIDE



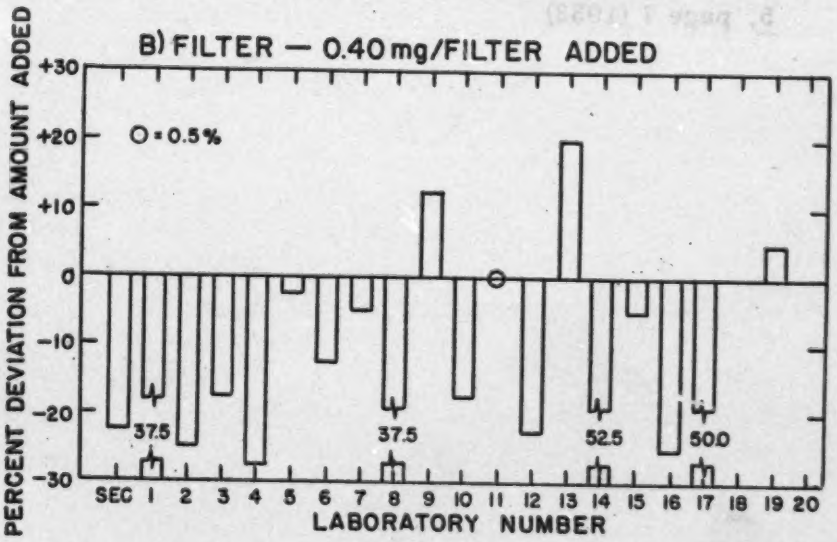
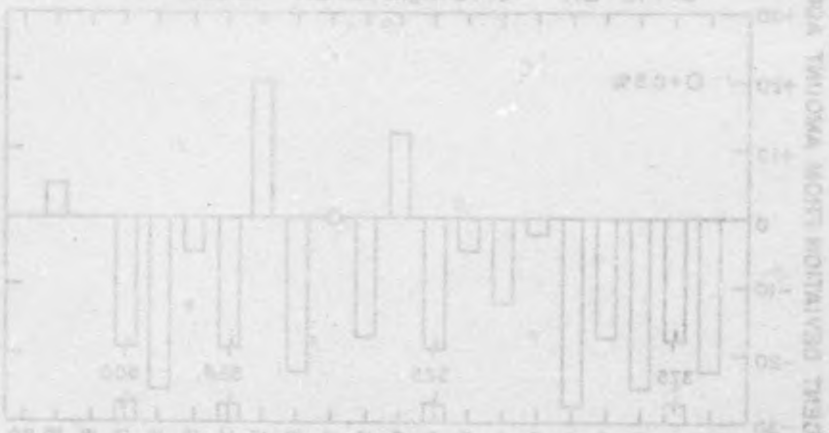


TABLE 7

KEY TO METHODS OF ANALYSIS FOR FLUORIDES

CODE	REFERENCE	METHOD
L	See Reference A-1	Megregian-Maier
M	See Reference A-1	Scott-Sanchis
N	Analytical Chemistry, 30, page 1009 (1958)	Eriochrome Cyanine R
	Analytical Chemistry, 29, page 1709 (1957)	Eriochrome Cyanine R
	Analytical Chemistry, 26, page 1161 (1954)	Eriochrome Cyanine R
O	See Reference A-1, page 105	Lamar
P	Analytical Chemistry, 30, page 2032 (1958)	SPADNS
Q	Analytical Chemistry, 26, page 996 (1954)	Thorium Nitrate
R	Industrial and Engineering Chemistry, 5, page 7 (1933)	Thorium Nitrate



COMMENTS ON FLUORIDE METHOD

Lab. 1 Method works very well. Minor deviations from the procedure may seriously affect the results. Not applicable to use by untrained personnel.

(METHOD L)

Lab. 2 The Megregian-Maier method gave consistent results and is a quick and simple procedure.

(METHOD L)

Lab. 3 Results obtained by distillation:

A .10 - .04 = .06/100 ml = .6 mg/liter
A .09 - .04 = .05/100 ml = .5 mg/liter
A .09 - .04 = .05/100 ml = .5 mg/liter

1.08 - .04 = .04/100 ml
2.08 - .04 = .04/100 ml/=.4 mg/filter
3.08 - .04 = .04/100 ml

Blank .04 mg Fl. Note: Distillation made with H_2SO_4 at 120°-130°C. It has been our experience that this method usually gives high results unless the blank is subtracted from it, as the blank runs high.

The color was evaluated in Nessler tubes and the difference between each succeeding standard is .01 mg-

The above results probably should be checked again, but we have no more solution left. We have in the past gotten erratic results using the acid distillation procedure, be it sulfuric acid or perchloric acid.

(METHOD M)

Lab. 4 Seems to be okay if the interfering ions are known and compensated for.

(METHOD M)

Lab. 5 We use the Megregian-Maier method because it is not time-consuming and since our regular samples do not contain interfering substances in effecting concentration, we feel it is an excellent method for our purpose. We routinely check all samples for chlorine and eliminate it if present. Occasionally, we find it necessary to use the distillation procedure.

(METHOD L)

COMMENTS ON FLUORIDE (Cont'd)

Lab. 6	No comments.	(METHOD L)
Lab. 7	No comments.	(METHOD N)
Lab. 8	"SPADNS" method of Bellack and Schouboe with sulfate correction.	(METHOD P)
Lab. 9	No comments.	(METHOD Q)
Lab. 10	Since chloride and sulfate values were not in excess and since preliminary tests showed excellent recovery of added fluoride in presence of the sample, the direct-reading Scott-Sanchis method was used. Had obvious interferences been present, the distillation procedure would have been used.	(METHOD M)
Lab. 11	Part 1 - Solution - A heavy growth of algae, identified as Chlorophyceae Dimorphococcus interfered with the direct Lamar method. A distillation procedure was necessary. Part II - Cloudiness due to filter papers interfered with direct method. May also have been responsible for losses encountered in all the determinations on the filters. Distillation procedure necessary on filters also.	(METHOD O)
Lab. 12	Satisfactory.	(METHOD L)
Lab. 13	No comments.	(METHOD M)
Lab. 14	This method is excellent for determining low concentrations of atmospheric fluorides. If the air concentration is above 50 ppb, it is necessary to make dilutions.	(METHOD Q)
Lab. 15	We use this method routinely with visual comparison. We did not distill any of the samples.	(METHOD M)
Lab. 16	No comments.	(METHOD O)
Lab. 17	No comments.	(METHOD R)
Lab. 18	No comments.	(METHOD -)

COMMENTS ON FLUORIDE (Cont'd)

Lab. 19 This method, similar to Megregian's for color development, eliminates sulfate interference by anion exchange. Since it was known that the sulfate concentration was below 50 ppm, the samples were not put through the resin with the results as recorded on the first page. When the samples were percolated through the resin,the following results were obtained:

Solution:	0.82 mg/l
Filter A:	0.37
B:	0.35 = 0.37 mg/filter
C:	0.40

(METHOD N)

Lab. 20 Fluorides not routinely done in this laboratory.

(METHOD -)

NITRATE

The data reported by the 21 participating laboratories have been divided into 5 groups of analytical methods. These data are summarized in Tabie 4, and shown graphically in Figure 4.

The average percent deviation from the amount added was 13.28% and 16.90% for the solution and filter samples respectively. The deviations of the individual laboratory results ranged from -39.6% to 16.7% and -84.3% to 17.9% for the solution and filter samples respectively.

Sixteen of the participating laboratories used the phenoldisulfonic acid method. The standard deviations were ±5.67 mg/l (18.5%) and ±2.76 mg/filter (22%) for the solution and filter samples respectively.. The large deviation associated with this method is in keeping with earlier ARS studies.

SUMMARY OF RESULTS

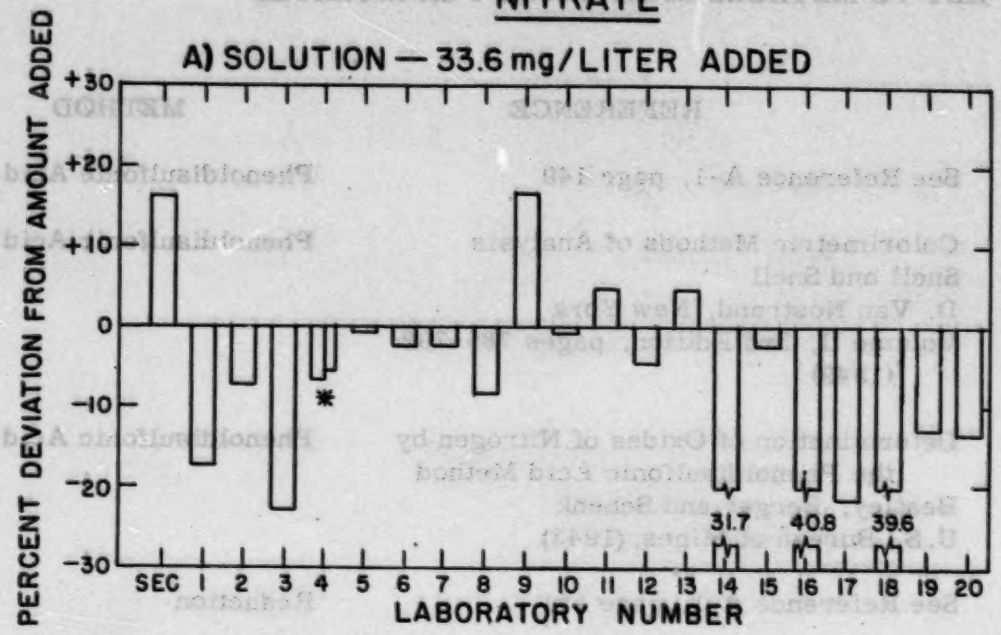
TABLE IV - NITRATE

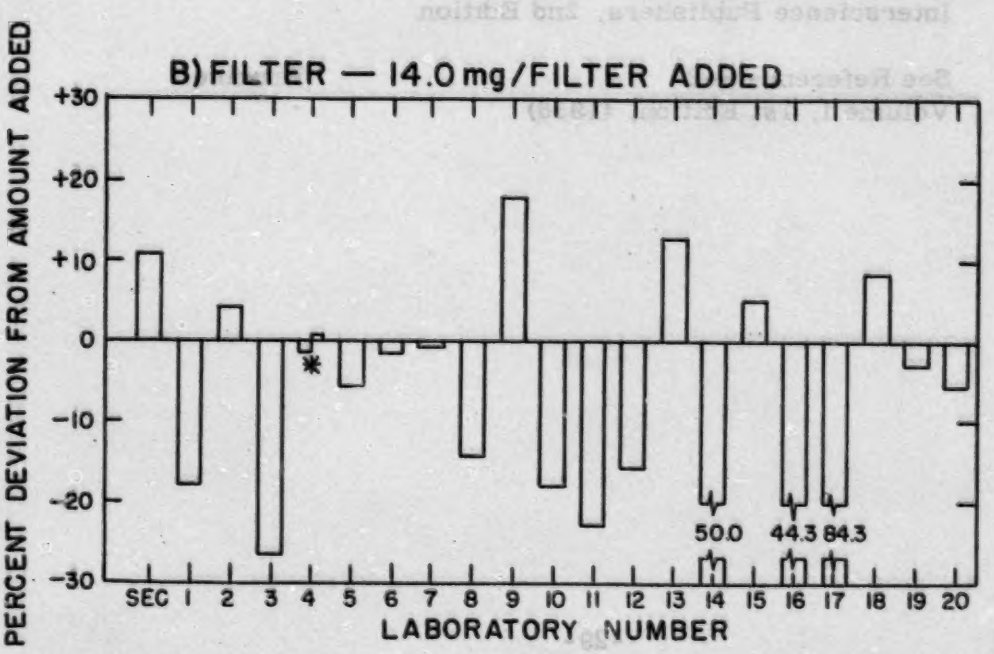
Type of Sample	Amount Added	Method	Number of Results Reported	Amount Reported			Percent Deviation From Amount Added	
				Average	Range	Standard Deviation	Average	Range
A) Solution	33.6 mg/liter	S	16	30.66	19.9 - 39.2	±5.67	14.04	-39.6 to +16.7
		T	2	29.05	26.4 - 31.7	-----	18.25	-21.4 to - 5.7
		U	2	31.10	29.3 - 32.9	-----	7.45	-12.8 to - 2.1
		V	1	32.8	----------	-----	2.4	----------
		W	1	29.2	----------	-----	13.1	----------
		Overall	22	30.59	19.9 - 39.2	±5.09	13.28	-39.6 to +16.7
B) Filter	14.0 mg/filter	S	16	12.57	7.0 - 16.5	±2.76	17.03	-50.0 to +17.9
		T	2	8.15	2.2 - 14.1	-----	42.50	-84.3 to + 0.7
		U	2	14.15	13.6 - 14.7	-----	3.95	- 2.9 to + 5.0
		V	1	13.9	----------	-----	0.7	----------
		W	1	13.2	----------	-----	5.7	----------
		Overall	22	12.4	2.2 - 16.5	±3.32	16.90	-84.3 to +17.9

FIGURE 4

ANALYTICAL REFERENCE SERVICE
SAMPLE TYPE IV (AIR INORGANIC)

NITRATE





* TWO METHODS USED

TABLE 8

KEY TO METHODS OF ANALYSIS FOR NITRATES

CODE	REFERENCE	METHOD
S-1	See Reference A-1, page 149	Phenoldisulfonic Acid
S-2	Colorimetric Methods of Analysis Snell and Snell D. Van Nostrand, New York Volume II, 3rd Edition, pages 785-792 (1949)	Phenoldisulfonic Acid
S-3	Determination of Oxides of Nitrogen by the Phenoldisulfonic Acid Method Beatley, Berger and Schenk U.S. Bureau of Mines, (1943)	Phenoldisulfonic Acid
T	See Reference A-1, page 151	Reduction
U	The Analyst, 75, page 388 (1950)	2, 4-Xylenol
V	Polarography Kolthoff and Lingane Interscience Publishers, 2nd Edition	Polarographic
W	See Reference S-2 Volume I, 1st Edition, (1936)	Brucine

COMMENTS ON NITRATE METHOD

Lab. 1	Very good method.	(METHOD S-1)
Lab. 2	The phenoldisulfonic acid method usually gives very consistent results. The results on this sample are not very consistent. The reason may be due to taking a very small aliquot because of the very high concentration of nitrate in the sample.	(METHOD S-1)
Lab. 3	The blank used was not the same as the one we use in actual practice. The absorbing solution used contains sulfuric acid and hydrogen peroxide and at times this blank may run high.	(METHOD S-1)
Lab. 4	The chloride interference with the phenoldisulfonic acid method seems to create quite a problem.	(METHODS T & S-1)
Lab. 5	No comments.	(METHOD S-1)
Lab. 6	No comments.	(METHOD S-1)
Lab. 7	No comments.	(METHOD V)
Lab. 8	No comments.	(METHOD S-1)
Lab. 9	No comments.	(METHOD S-3)
Lab. 10	Directions for extraction of filters resulted in partial disintegration of the paper and produced an opalescent solution obviously unsuited for turbidimetric sulfate determination and visual reading of fluoride (Scott-Sanchis method). Clarification was accomplished by filtration through Whatman #30 filter paper.	(METHOD S-1)
Lab. 11	See Fluorides. Algae may have been responsible for high results on solution.	(METHOD S-1)
Lab. 12	Accurate.	(METHOD S-1)
Lab. 13	No comments.	(METHOD S-1)

COMMENTS ON NITRATE (Cont'd)

Lab. 14 The accuracy of this method is dependent on removal of other ions that will be found in an atmospheric sample. The time necessary for analysis by the laboratory staff is excessive. Therefore, other methods are being investigated. **(METHOD S-1)**

Lab. 15 This method seems to work quite well. **(METHOD U)**

Lab. 16 Approximately 2½ months elapsed from the time sample was received to date of analysis. Therefore any nitrites or ammonia present would be converted to nitrates - making our results high. Nitrates were heavy on 100 mls of sample used for analysis. **(METHOD S-1)**

Lab. 17 No comments. **(METHOD T)**

Lab. 18 No comments. **(METHOD S-2)**

Lab. 19 No comments. **(METHOD U)**

Lab. 20 We find the method, nitrates by brucine, simpler and more rapid for the routine analysis of large numbers of samples. **(METHOD W)**

SUMMARY OF LABORATORY DATA

Lab No.	Results	Average Amt. Reported	% Deviation From Amt. Added	Method
SEC	36.5 36.8 36.4	36.6	-4.7	A-1
1	41.5 41.5 41.7	41.6	+8.3	C
2	56 56 54	55.3	+44.0	C
3	31.0 30.0 27.0	29.3	-23.7	B
4	38.3 38.3 38.8	39.5	+2.9	A-1
5	40 40 40	40.0	+4.2	C
6	37 37 37	37.0	-3.6	D
7	41.2 40.3 42.0	41.2	+7.3	C
8	31.3 32.3 ----	31.3	-18.5	A-1
9	44.4 46.1 46.9	45.8	+19.3	A-2

TABLE 9

SULFATE

A) Solution - 38.4 mg/liter added

Lab No.	Results	Average Am't. Reported	% Deviation From Am't. Added	Method
SEC	36.5 36.8 36.4	36.6	-4.7	A-1
1	41.5 41.5 41.7	41.6	+8.3	C
2	56 56 54	55.3	+44.0	C
3	31.0 30.0 27.0	29.3	-23.7	B
4	39.3 39.3 39.9	39.5	+2.9	A-1
5	40 40 40	40.0	+4.2	C
6	37 37 37	37.0	-3.6	D
7	41.2 40.3 42.0	41.2	+7.3	C
8	31.3 32.3 ----	31.3	-18.5	A-1
9	44.4 46.1 46.9	45.8	+19.3	A-2

TABLE 9 - Sulfate - Cont'd.

Lab. No.	Results	Average Am't. Reported	% Deviation From Am't. Added	Method
10	37.5 37.5 37.5	37.5	-2.9	B
11	38.0 40.0 ----	39.0	+1.6	C
12	46 45 47	46.0	+19.8	E
13	44.4 41.6 43.0	43.0	+12.0	A-1
14	45.0 44.4 44.4	44.6	+16.1	A-1
15	31.0 31.0 32.0	31.3	-18.5	B
16	38.1 38.7 ----	38.4	0.0	A-1
17	37.8 39.2 37.7	38.2	-0.5	A-1
18	39.0 40.7 40.7	39.9	+3.9	B
19	39 35 31	35.0	-8.9	B
20	38.5 38.5 38.5	38.5	+0.3	B

TABLE 10

SULFATE

B) Filter - 16.0 mg/filter Added

Lab. No.	Results	Average Am't. Reported	% Deviation From Am't. Added	Method
SEC	15.4 13.9 15.4	14.8	-7.5	A-1
1	14.0 14.5 14.5	14.3	-10.6	C
2	23 22 22	22.3	+37.5	C
3	14.5 13.5 14.0	14.0	-12.5	B
4	16.8 17.6 16.8	17.1	+6.9	A-1
5	18.5 17.0 19.0	18.2	+13.8	C
6	14 14 14	14.0	-12.5	D
7	16.5 16.3 16.5	16.4	+2.5	C
8	16.5 16.4 15.8	16.2	+1.3	A-1
9	18.1 17.3 17.7	17.7	+10.6	A-2

TABLE 10 - Sulfate - Cont'd.

Lab No.	Results	Average Am't. Reported	% Deviation From Am't. Added	Method
10	14.8	14.9	-6.8	B
	14.0			
	16.0			
11	15.0	14.0	-12.5	C
	13.0			
	13.5			
12	17.0	17.5	+9.4	E
	18.0			
	17.5			
13	20.3	20.5	+28.1	A-1
	21.3			
	20.1			
14	13.0	12.8	-20.0	A-1
	12.5			
	13.0			
15	15.0	15.0	-6.2	B
	15.0			
	15.0			
16	15.5	16.2	+1.3	A-1
	16.7			
	16.4			
17	14.7	14.9	-6.9	C
	15.0			
	15.0			
18	16.5	16.6	+3.8	B
	16.9			
	16.5			
19	13.9	13.9	-13.1	B
	13.4			
	14.3			
20	15.5	15.7	-1.9	B
	15.8			
	15.8			

TABLE 11

CHLORIDE

A) Solution - 14.4 mg/liter Added

Lab No.	Results	Average Am't. Reported	% Deviation From Am't. Added	Method
SEC	14.3 14.0 13.8	14.0	-2.8	F
1	18 19 19	18.6	+29.2	F
2	14 14 16	14.7	+2.1	F
3	11.6 11.0 19.0	12.2	-15.3	K
4	14 14 14	14.0	-2.8	G
5	16.0 17.0 18.0	17.0	+18.1	G
6	18 18 18	18.0	+25.0	H
7	13.7 13.9 13.6	13.6	-5.6	J
8	14.9 15.1 15.0	15.0	+4.2	G
9	13.41 13.41 13.41	13.4	-6.9	G

TABLE 11 - Chloride - Cont'd.

Lab. No.	Results	Average Am't. Reported	% Deviation From Am't. Added	Method
10	14.3 14.0 14.0	14.1	-2.1	F
11	14.0 14.0 14.0	14.0	-2.8	F
12	18 18 18	18.0	+25.0	F
13	20 20 20	20.0	+38.9	F
14	14.8 13.9 14.4	14.3	-0.7	G
15	18.0 18.0 17	17.7	+22.9	I
16	17.7 17.7 ----	17.7	+22.9	F
17	17 17 17	17	+18.1	F
18	14.5 14.0 14.0	14.2	-1.4	I
19	14.1 14.0 13.9	14.0	-2.8	I
20	15.0 15.0 15.5	15.2	+5.5	I

TABLE 12

CHLORIDE

B) Filter - 6.0 mg/filter Added

Lab No.	Results	Average Am't. Reported	% Deviation From Am't. Added	Method
SEC	7.05 6.10 5.88	5.3	-8.3	F
1	9.5 9.5 7.0	8.7	+45.0	F
2	5 7 7	6.0	0.0	F
3	4.5 4.8 4.8	4.7	-21.7	K
4	6 6 6	6.0	0.0	G
5	7.0 7.0 6.5	6.8	+13.4	G
6	8 8 8	8.0	+33.4	H
7	5.1 4.9 5.3	5.1	-15.0	J
8	7.35 7.10 7.30	7.2	+20.0	G
9	6.0 5.8 5.8	5.9	-1.6	G

TABLE 12 - Chloride - Cont'd.

Lab No.	Results	Average Am't. Reported	% Deviation From Am't. Added	Method
10	5.8 5.9 6.0	5.9	-1.6	F
11	6.5 5.8 5.7	6.0	0.0	F
12	8.6 8.6 8.6	8.6	+43.4	F
13	10.0 10.0 9.8	9.9	+63.4	F
14	6.9 7.0 6.9	6.9	+15.0	G
15	6.8, 6.5 6.8, 6.5 7.5, 8.2 7.0, 7.0 8.0	7.7	+28.4	I
16	8.3 8.3 8.3	8.3	+38.4	F
17	7.5 7.5 7.5	7.5	+25.0	F
18	6.8 6.8 6.3	6.6	+10.0	I
19	6.5 6.4 6.8	6.6	+8.4	I
20	6.5 6.8 6.3	6.5	+8.4	I

TABLE 13

FLUORIDE

A) Solution - 0.96 mg/liter Added

Lab No.	Results	Average Am't. Reported	% Deviation From Am't. Added	Method
SEC	1.02 1.03 1.10	1.05	+9.4	L
1	1.0 1.0 1.0	1.00	+4.2	L
2	0.95 0.95 1.10	1.00	+4.2	L
3	0.9 0.9 0.9	0.90	-6.2	M
4	0.94 0.95 0.94	0.94	-2.1	M
5	1.02 1.04 1.04	1.03	+7.3	L
6	1.0 1.1 1.0	1.03	+7.3	L
7	0.86 0.95 0.97	0.93	-3.1	N
8	1.03 1.03 1.03	1.03	+7.3	P
9	1.15 1.28 1.46	1.30	+35.4	Q

TABLE 13 - Fluoride - Cont'd.

Lab No.	Results	Average Am.t Reported	% Deviation From Am't. Added	Method
10	0.88 0.88 0.88	0.88	-8.3	M
11	1.00 1.02 1.02	1.02	+6.3	O
12	1.0 1.0 1.0	1.00	+4.2	L
13	0.96 0.98 0.98	0.97	+1.0	M
14	0.20 0.20 0.20	0.20	-79.1	Q
15	0.94 0.94 0.94	0.94	-2.1	M
16	1.2 1.0 0.7	0.97	+1.0	O
17	0.57 ---- ----	0.57	-40.6	R
18	---- ---- ----	---	---	-
19	0.95 0.95 0.95	0.95	-1.0	N
20	---- ---- ----	---	---	-

TABLE 14

FLUORIDE

B) Filter - 0.40 mg/filter Added

Lab No.	Results	Average Am't. Reported	% Deviation From Am't. Added	Method
SEC	0.34 0.30 0.30	0.31	-22.5	L
1	0.28 0.28 0.28	0.25	-37.5	L
2	0.33 0.28 0.28	0.30	-25.0	L
3	0.30 0.35 0.35	0.33	-17.5	M
4	0.29 0.39 0.24	0.29	-27.5	M
5	0.39 0.39 0.39	0.39	-2.5	L
6	0.35 0.35 0.35	0.35	-12.5	L
7	0.38 0.39 0.38	0.38	-5.0	N
8	0.25 0.25 0.25	0.25	-37.5	P
9	0.44 0.46 ----	0.45	+12.5	Q

TABLE 14 - Fluoride - Cont'd.

Lab No.	Results	Average Am't. Reported	% Deviation From Am't. Added	Method
10	0.33 0.34 0.33	0.33	-17.5	M
11	0.40 0.41 0.39	0.40	0.0	O
12	0.30 0.30 0.35	0.31	-22.5	L
13	0.45 0.45 0.44	0.45	+12.5	M
14	0.19 0.19 0.19	0.19	-52.5	Q
15	0.38, 0.38 0.38, 0.38 0.38, 0.38 0.38, 0.38 0.38	0.38	-5.0	M
16	0.3 0.3 0.3	0.30	-25.0	O
17	0.22 0.18 0.20	0.20	-50.0	R
18	---- ---- ----	---	---	-
19	0.43 0.40 0.44	0.43	+5.0	N
20	---- ---- ----	---	---	-

TABLE 15

NITRATE

A) Solution - 33.6 mg/liter Added

Lab No.	Results	Average Am't. Reported	% Deviation From Am't. Added	Method
SEC	39 39 39	39.0	+16.1	S-1
1	23.9 29.7 29.7	27.8	-17.3	S-1
2	25.7 34.6 33.2	31.2	-7.1	S-1
3	26.1 25.9 25.9	25.9	-22.9	S-1
4	31.5, 31.4 31.1	31.3	-6.8	S-1
	32.4, 31.0 31.6	31.7	-5.7	T
5	34 33 33	33.3	-0.9	S-1
6	32.4 32.4 33.6	32.8	-2.4	S-1
7	33.2 32.6 32.6	32.8	-2.4	V
8	30.3 31 31	30.8	-8.3	S-1
9	39.4 39.4 38.8	39.2	+16.7	S-3

TABLE 15 - Nitrate - Cont'd.

Lab No.	Results	Average Am't. Reported	% Deviation From Am't. Added	Method
10	34.0	33.3	-0.9	S-1
	32.0			
	34.0			
11	35.2	35.2	+4.8	S-1
	35.2			
	35.2			
12	32.1	32.1	-4.5	S-1
	32.1			
	32.1			
13	35.2	35.2	+4.8	S-1
	35.2			
	35.2			
14	23.3	23.3	-30.7	S-1
	23.3			
	23.3			
15	33.9	32.9	-2.1	U
	33.9			
	30.0			
16	23.13	19.9	-40.8	S-1
	17.71			

17	26.4	26.4	-21.4	T
	26.4			
	26.4			
18	20.3	20.3	-39.6	S-2
	20.3			
	20.3			
19	31.5	29.3	-12.8	U
	28.5			
	28.0			
20	28.2	29.2	-13.1	W
	29.2			
	30.2			

TABLE 16

NITRATE

B) Filter - 14.0 mg/filter Added

Lab No.	Results	Average Am't. Reported	% Deviation From Am't. Added	Method
SEC	15.9 15.5 15.1	15.5	+10.7	S-1
1	10.6 12.0 12.0	11.5	-17.9	S-1
2	13.7 14.2 15.9	14.6	+4.3	S-1
3	10.4 10.3 10.2	10.3	-26.4	S-1
4	13.8 13.3 14.2	13.8	-1.4	S-1
	14.3 14.1 13.4	14.1	+0.7	T
5	13.0 13.0 13.5	13.2	-5.7	S-1
6	13.8 13.6 13.8	13.8	-1.4	S-1
7	14.1 14.1 13.6	13.9	-0.7	V
8	12.0 11.1 13.0	12.0	-14.3	S-1
9	16.4 18.1 15.1	16.5	+17.9	S-3

TABLE 16 - Nitrate - Cont'd.

Lab. No.	Results	Average Am't. Reported	% Deviation From Am't. Added	Method
10	11.5 11.5 11.5	11.5	-17.9	S-1
11	10.6 10.6 11.4	10.8	-22.9	S-1
12	12.8 12.8 14.5	13.1	-15.8	S-1
13	15.4 16.3 16.3	15.8	+12.9	S-1
14	7.7 5.8 7.7	7.0	-50.0	S-1
15	15 15.5 14.5, 14.5 15 14.5 14.0, 14.0 15.0	14.7	+5.0	U
16	6.64 8.85 7.97	7.8	-44.3	S-1
17	2.2 2.2 2.2	2.2	-84.3	T
18	15.5 15.5 14.7	15.2	+8.6	S-2
19	14.0 13.5 13.3	13.6	-2.9	U
20	13.6 13.2 12.8	13.2	-5.7	W